

FUNCTIONAL PROPERTIES OF THREE NATIVE STARCHES AND THEIR
MODIFIED DERIVATIVES*Funmilayo Deborah Adewumi, Labunmi Lajide, Abayomi Olagunjoye Adetuyi, Olajide Ayodele***ABSTRACT**

Starches were isolated from cocoyam (*Xanthosoma sagittifolium*), white yam (*Dioscorea rotundata*) and bitter yam (*Dioscorea dumetorum*). Starch modification was carried out using acetic anhydride and phthalic anhydride. The native and modified starches were characterized using Fourier Transformed Infra-red Spectroscopy (FTIR) for identification of the functional groups. Functional properties such as water absorption capacities, oil absorption capacity, swelling power, solubility, gelation temperature, least gelation capacity, amylose content and pH were determined using standard procedures. Acetylation increased the water absorption capacity, oil absorption capacity, swelling power, amylose content, and solubility of the starches while phthalation decreased water absorption capacity, oil absorption capacity, swelling power, and solubility of the starches. Native cocoyam starch has the highest gelation temperature (85 °C) while Acetylated bitter yam has the lowest gelation temperature (74 °C). The pH of the native and modified starches was within the range of 4.14 – 6.55. Phthalation and acetylation increased the bulk density of the starches. Native cocoyam, white yam, and bitter yam starches had the lowest gelation concentration (6%). Modification of native starches will improve the usage of starch in food and non-food applications.

Keywords: native starch; phthalation; gelation; amylose; pregelatinized starch

INTRODUCTION

Starch is one of the most available natural polymers is a starting material or an intermediate for many chemical industries (Yadav and Garg, 2013). Starch is a useful raw material for adhesive industries because of its availability and abundance (Yu et al., 2009). Starch has been applied as a filler and bonding agent in the making of tablets, it is also used as an additive to improve the shelf life of soaps and detergents. Other uses of starch are in the rubber and foam industries (Tonukari, 2004) and the food industry (Dura and Rosell, 2016).

In the food sector, starch is being used to give divers functionalities which include stabilizing, gelling, encapsulating, thickening, texturing, and shelf-life elongation. Despite the numerous advantageous properties in chemical industries, however, many starches in their crude form have limited applications in industrial processes as they have a high level of retrogradation which limits their application in food processing industries (Singh, Kaur and Singh, 2004). However, it is necessary to modify crude starches to incorporate some specific properties which thereafter make them useful in the industrial sector (Torruco-Uco and Betancur-Ancona, 2007).

Cocoyam (*Colocasia esculenta*) which is an ancient tuber of *Araceae* family originated from South-East, Asia, and

has been cultivated for over 2000 years (Wang, Truong and Wang, 2003). It has both red and white varieties. White yam (*Dioscorea rotundata*) is widely cultivated in Africa as an edible tuber with economic importance (Omonigbo and Ikenebomeh, 2000). Bitter yam (*Dioscorea dumetorum*) belongs to *Dioscoreaceae* family. It is rich in phyto-nutrients such as proteins (Medoua et al., 2005); still, it remains one of the underutilized tropical tubers in the world (Owuamanam et al., 2013).

The present study focuses on the modification of four different starches using acetylation and phthalation processes, and also the determination of the functional properties of both native and the modified starches.

Scientific hypothesis

This research evaluated the significance of chemical modifications of native starches and the subsequent effects by comparing the characterizations and properties with their modified derivatives.

MATERIAL AND METHODOLOGY**Materials**

Cocoyam, white yam, and bitter yam (Figure 1) were bought from a local market in Ado-Ekiti, Ekiti State, Nigeria. All the reagents used were of analytical grade.



Figure 1 Pictorial representations of cocoyam (A), white yam (B) and bitter yam (C).

Starch Isolation: The starches were isolated using the wet extraction method as described by (Shujun et al., 2006). The tubers were thoroughly washed with water, cut into small sizes, and homogenized blended for about five minutes. The produced slurry was transferred into a muslin cloth and released into a bucket with distilled water. The content was continuously squeezed to eject the starch into the bucket of water, the starch was allowed to settle overnight and the supernatant was decanted. The product was rinsed continuously to remove soluble impurities until the supernatant was clear, the final product was spread on a flat substrate and air-dried.

Preparation of acetylated starches

The method of (Sathe and Salunkhe, 1981) was employed in the acetylation process. 100 g of starch was measured and dispersed in 500 mL distilled water, the resulting mixture was magnetically stirred for 20 min. The pH of the obtained slurry was adjusted to 8.0 using 1 M NaOH. 10.2 g of acetic anhydride was added for a period of 1 h, and the reaction was allowed to proceed for 5 min after the addition of acetic anhydride. The pH of the slurry was then adjusted to 4.5 using 0.5 M HCl. The product was filtered, washed several times with distilled water, and air-dried.

Preparation of Pregelatinized Starch Phthalate

Pre-gelatinized Starch Phthalate was prepared using the method of (Surini, Ssputri and Anwar, 2014). Two basic steps were involved: gelatinization and esterification. Gelatinization was carried out by heating starch solution at 70 °C, the gel was then oven-dried, ground, and sieved. The esterification reaction was done by reacting 10% pre-gelatinized starch in distilled water with 16.7% solution phthalic anhydride in 96% ethanol. 10 M NaOH was added

continuously during the reaction to keep the pH between 8 and 10. Anhydrous sodium sulphate was added to absorb excess moisture. Stirring was carried out at 1000 rpm, the stirring was continued for 30 more minutes and allowed to stay for 24 h. The mixture pH was adjusted to 6.5 – 7.0 using HCl solution. 50% Ethanol was added into the neutralized solution to wash the un-reacted phthalate. The final precipitate was dried, ground, and sieved to obtain pre-gelatinized starch phthalate (PCSP) powder.

Fourier Transform Infrared (FT-IR) Analysis

The functional groups of native and modified cocoyam, bitter yam, and white yam starches were obtained using Fourier Transform Infra-Red (Shimadzu Model FTIR – 8201PC).

FUNCTIONAL PROPERTIES

Water absorption capacity (WAC)

Water absorption capacity was carried out using the method described by (Omojola et al., 2010). One gram of the sample was mixed with 10 mL distilled water for 5 min. The sample was allowed to stay for 30 min, centrifuged at 3000 rpm for 30 min, the volume of the supernatant was measured. Assuming the density of distilled water was 1 g.mL⁻¹.

Swelling power and solubility

Swelling power and solubility were determined using the method described by (Awokoya et al., 2011). One gram of native starch was weighed and transferred into a clean and dried test tube (W1). The native starch was dispersed in distilled water (20 mL). The obtained slurry was heated at 60 °C for 30 min in a calibrated water bath. The mixture was centrifuged at 3000 rpm for 20 min, the supernatant was decanted and the swollen granules were weighed

(W₂). 10 mL of the supernatant was oven-dried at 120 °C. The residue obtained on drying the supernatant indicates the quantity of starch solubilized. The swelling and solubility are calculated as follows:

$$\text{Swelling of starch (g/g)} = \frac{W_2 - W_1}{\text{weight of starch}}$$

$$\text{Solubility of Starch (g/g)} = \frac{\text{weight of dried aliquot}}{\text{weight of starch}}$$

Gelatinization temperature (GT)

Gelatinization temperature was determined by the method described by (Attama et al., 2003). About 1 g of starch sample was transferred into a beaker and 10 mL of distilled water was added. The dispersion was heated on a hot plate. The gelatinization temperature was then taken with a thermometer suspended in the slurry.

Determination of least gelation concentration

The method of (Sathe and Solunkhe, 1981) was used with slight modification. Appropriate sample suspensions of 2, 4, 6, 8, 10, 12, 14, 16 w.v⁻¹ were prepared in 5 mL distilled water. The test tubes containing the suspensions were heated for 1 h in boiling water cooled under running tap water. The least gelation concentration was determined as concentration when the sample from the inverted test tube did not fall down or slip.

Determination of bulk density

Bulk density was determined using the procedure of (Gbadamosi and Oladeji, 2013) with slight modification. The sample (10 g) was put into a 100 mL graduated cylinder. The cylinder was tapped forty times and the bulk density was calculated as weight per unit volume (g.mL⁻¹)

$$\text{Bulk density (g/mL)} = \frac{W_2 - W_1}{V}$$

pH Determination

The pH was determined using the procedure of (Omojola et al., 2012). 20 g of the sample was shaken in 100 mL of distilled water for 5 min and the pH was determined using a pH meter.

Amylose content

The amylose content of the samples was determined by the colorimetric measurement of the blue amylose-iodine complex (Mir, Srikaeo and García, 2013). In summary, 100 mg of sample was weighed into a 100 mL volumetric flask, mixed with 1 mL ethanol and 9 mL of 2 M NaOH. The samples were diluted and the iodine solution was added. After 10 min incubation at room temperature, the absorbance at 620 nm was analyzed using UV-spectrophotometer (Beckman DU640 UV/Vis Spectrophotometer) and the amylose content was calculated based on the standard curve. The samples were analyzed in triplicate.

Statistical analysis

All the analyses were done in triplicate and the data were statistically subjected to Analysis of Variance (ANOVA) using SPSS (IBM Statistics 21). Results are means of

replicates (determined on a dry weight basis) ± standard deviation, significantly different at $p < 0.05$.

RESULTS AND DISCUSSION

FTIR spectroscopy was used to verify the changes in the chemical structures of starch molecules resulting from acetylation and phthalation. The FTIR spectra of native, acetylated and phthalated cocoyam starches are presented in Figure 2, Figure 3, and Figure 4. In the spectrum of native starch, the peak at 3421.72 cm⁻¹ and 2929.87 cm⁻¹ correspond to O-H and C-H stretching, while the peaks at 1654.92 cm⁻¹ and 1458.18 cm⁻¹ correspond to O-H and C-H bending. Acetylated starches show new strong absorption bands at 1732.08 cm⁻¹; this indicates C=O stretching of acetyl group. Mano, Koniarova and Reis (2003) submitted a similar report. Phthalated starch showed new absorption bands at 1849.73 cm⁻¹, this new absorption indicates that phthalated starches were formed during the esterification process.

The FTIR spectra of native, acetylated and phthalated white yam starches are presented in Figure 5, Figure 6, and Figure 7. For the native starch, the peak at 3423.65 cm⁻¹ and 2929.87 cm⁻¹ correspond to O-H and C-H stretching, while the peaks at 1653.00 cm⁻¹ and 1458.18 cm⁻¹ correspond to O-H and C-H bending. Acetylated and the phthalated white yam starch did not show a new absorption band.

The FTIR spectra of native, acetylated and phthalated bitter yam starches are presented in Figure 8, Figure 9 and Figure 10. For native starch, the peaks at 3394.72 cm⁻¹ and 2929.87 cm⁻¹ correspond to O-H and C-H stretching, while the peaks at 1654.92 – 1637.56 cm⁻¹ and 1438.18 cm⁻¹ corresponds to O-H and C-H bending. Acetylated starches show new strong absorption bands at 1909.53 cm⁻¹; this indicates C=O stretching of acetyl group. Phthalated starch showed new absorption bands at 1703.14 cm⁻¹ due to the carbonyl group of esters.

The results of the functional properties of native and modified starches are presented in Table 1. Native cocoyam starch has a water absorption capacity (WAC) of 8.70 ± 0.02 g.g⁻¹, the value was increased after acetylation (9.37 ± 0.15), and reduced after phthalation (6.50 ± 0.30). The WAC values for native white yam and bitter yam starches were 8.17 ± 0.15 and 8.94 ± 0.05 g.g⁻¹, respectively, however, the values were increased (8.87 ± 0.15, 8.50 ± 0.01 g.g⁻¹) after acetylation and decreased (5.33 ± 0.50 and 4.56 ± 0.21 g.g⁻¹) after phthalation. Acetylated white yam starch showed the highest water absorption capacity while the phthalated bitter yam showed the least WAC. Acetylation increased the WAC of all the starches compared to their corresponding native starches, whereas phthalation decreased the WAC. A similar increase in the WAC upon acetylation was obtained in acetylated starches of sweet potato (Lee and Yoo, 2009) and corn (Diop et al., 2011). The increase in the WAC in acetylated starches could be associated with the introduction of acetyl groups that impeded intermolecular chain associations, causing structural disorganization that facilitated water access in the amorphous region (Xu, Dzenis and Hanna, 2005).

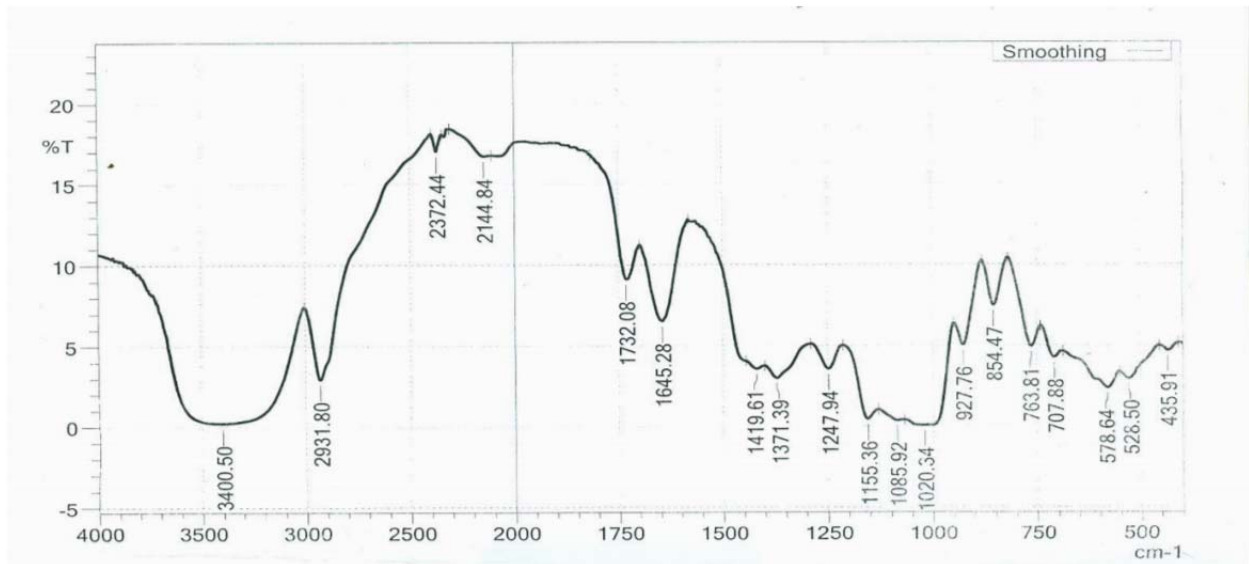


Figure 2 FTIR spectrum of native Cocoyam starch.

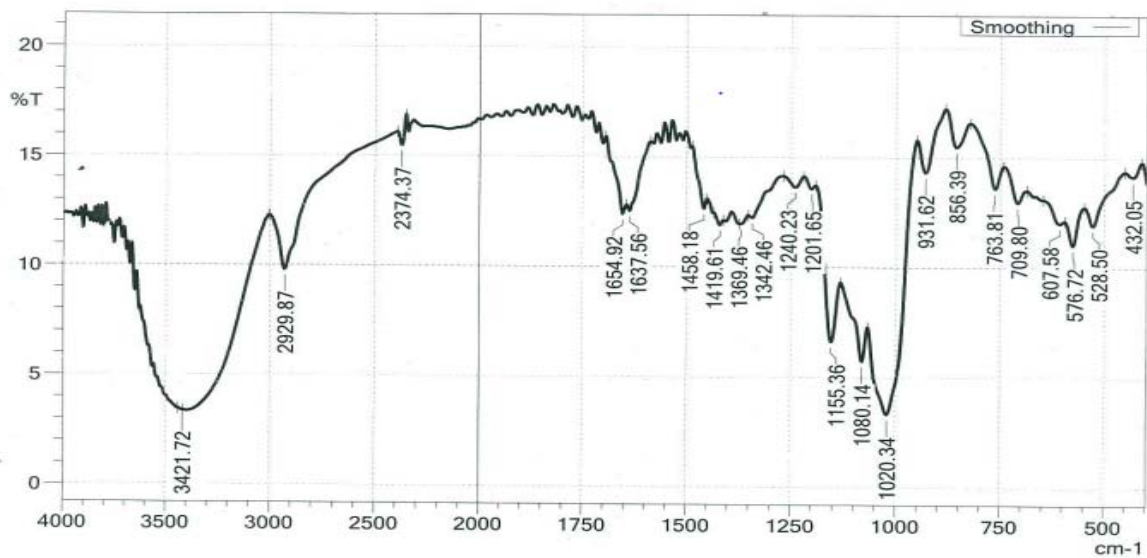


Figure 3 FTIR spectrum of acetylated Cocoyam starch.

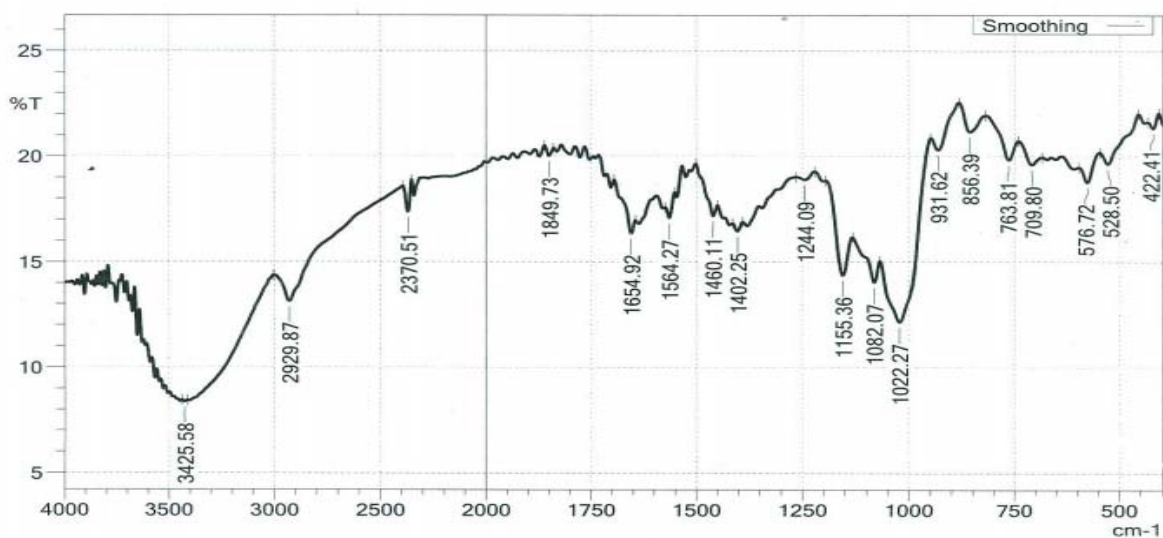


Figure 4 FTIR spectrum of phthalated Cocoyam starch.

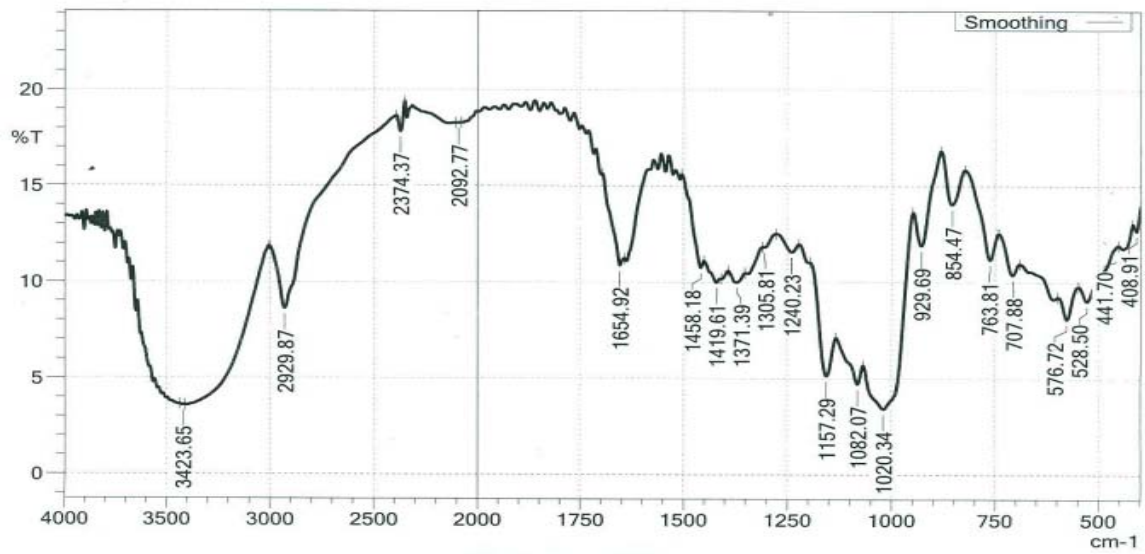


Figure 5 FTIR spectrum of native White yam starch.

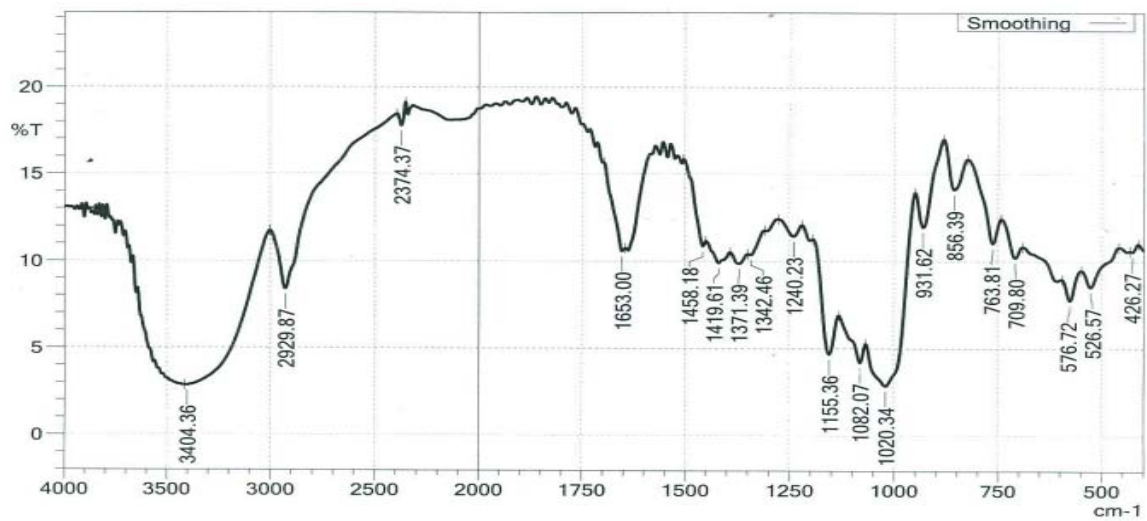


Figure 6 FTIR spectrum of acetylated White yam starch.

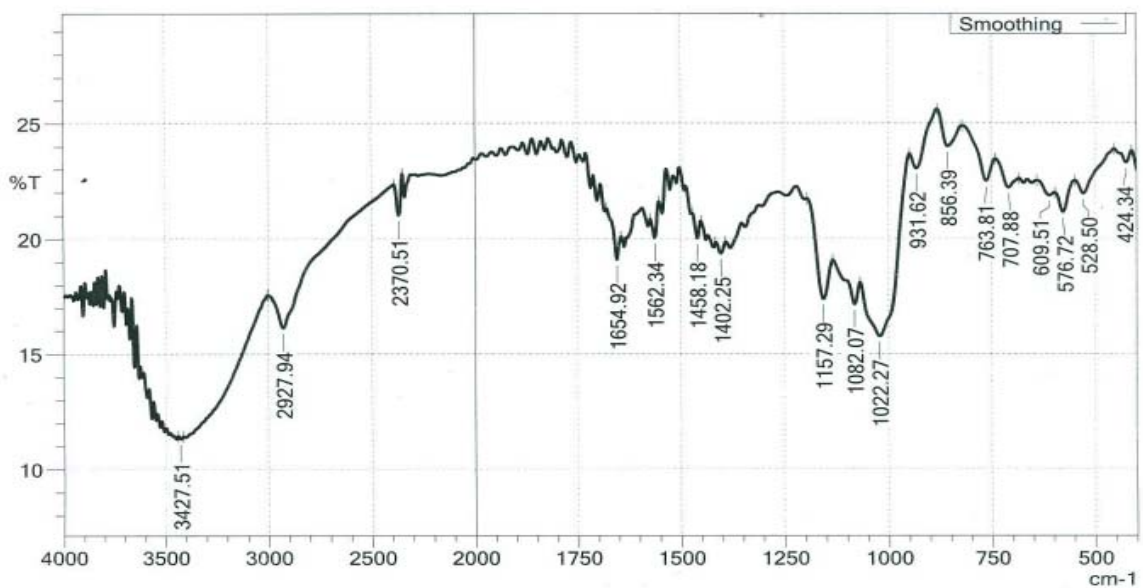


Figure 7 FTIR spectrum of phthalated white yam starch.

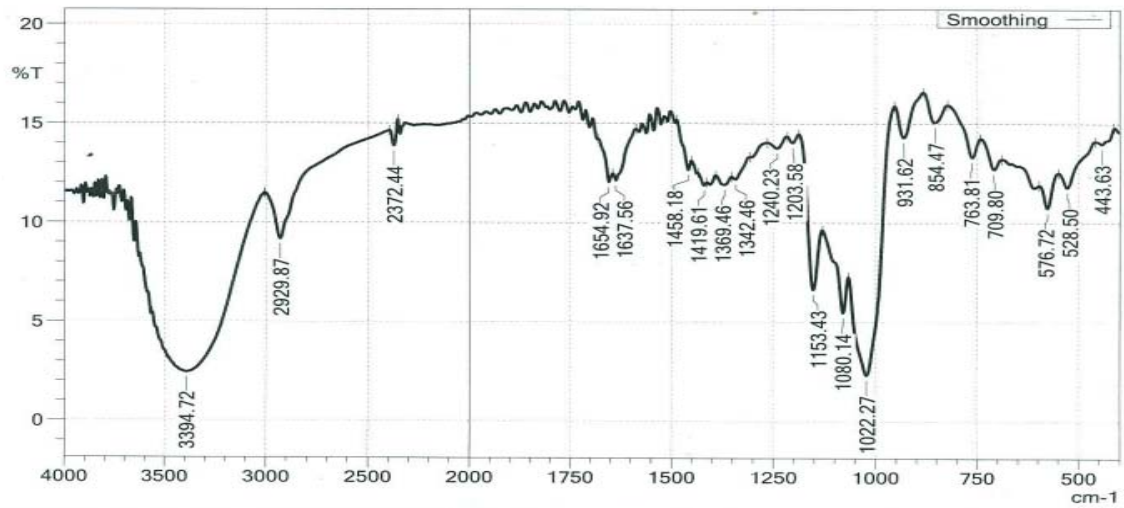


Figure 8 FTIR of sample native bitter yam starch.

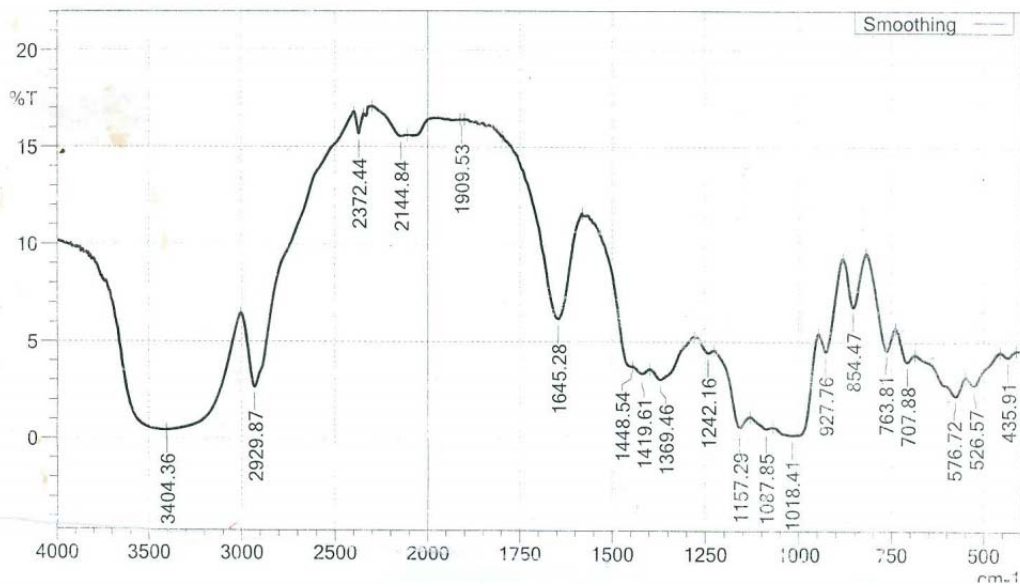


Figure 9 FTIR of acetylated bitter yam starch.

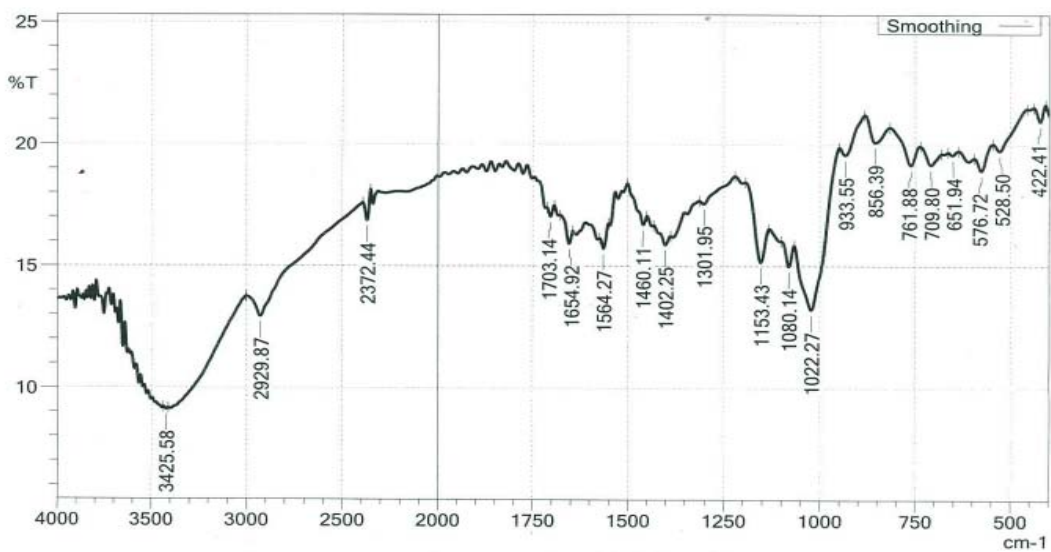


Figure 10 FTIR of sample phthalated bitter yam starch.

A decrease in WAC in phthalated starches could be that phthalation reinforces the structure of starch granules and limit water absorption which restricts the mobility of starch chain in the amorphous region (**Gunaratne and Corke, 2007**). An increase in water absorption capacity of acetylated starches gave it the advantage of being used as a thickener in liquid and semi-liquids foods, it could be used in the development of confectionery products such as hard candies, the acetylated starches could also be used to produce absorbent materials such as disposable diapers and female napkins. The decreased water absorption capacity of phthalated starches suggests that they could be used in biodegradable films because of their reduction in hydrophilic property.

In the case of oil absorption capacity (OAC), Native cocoyam starch has an OAC of 2.57 ± 0.21 which increased after acetylation ($3.33 \pm 0.42 \text{ g.g}^{-1}$) and reduced after phthalation $1.63 \pm 0.25 \text{ g.g}^{-1}$. The OAC of the native white yam and bitter yam were 3.47 ± 0.06 and $3.62 \pm 0.20 \text{ g.g}^{-1}$, respectively. However, the OAC values increased after acetylation and decreased after phthalation. Acetylated white yam starch showed the highest oil absorption capacity and phthalated cocoyam showed the least OAC. Acetylation increased the OAC of all the starches compared to their corresponding native starches, whereas phthalation decreased the OAC. This result suggested that acetylation enhanced the hydrophobic tendencies of the starches. A similar result was reported by **Uzomah and Ibe, (2011)**. WHO indicated that Acetylated starches had the strongest affinity for oil absorption. The obtained results showed that acetylation could be used to improve the oil absorption capacity of native starches.

Swelling power and solubility centre on the interaction between starch chains within the amorphous and crystalline regions, and the results are presented in Table 1. The swelling power of the native cocoyam, white yam, and native bitter yam starches increased after acetylation and decreased after phthalation. Acetylated bitter yam showed the highest swelling power while ($4.63 \pm 0.15 \text{ g.g}^{-1}$) while phthalated white yam starch ($1.64 \pm 0.04 \text{ g.g}^{-1}$) has the least swelling property. Increase observed in the swelling power of acetylated starches may be due to the weakening and disrupting of intra- and inter molecular hydrogen bonds in the starch chains, which may increase the accessibility of the starch granules to water. (**Lee and Yoo, 2009; Olu-Owolabi et al., 2014**). Similar reports on swelling power after modifications have been documented (**Olayinka, Adebowale and Olu-Owolabi, 2013**). The reduction in swelling power after phthalation could be linked to the possible structural disintegration within the starch matrix as a result of the modification. **Lawal (2004); Adebowale and Lawal (2003)** reported that the lower swelling power of phthalated starches denotes the stability of starch granule. Starch swelling power is very important in the formulation of tablets and capsules, it is conceived that disintegrant works through swelling action (**Adebayo and Itiola, 1998**). Consequently, starch with high swelling power is expected to release active pharmaceutical ingredients at a faster rate. Also, high swelling power leads to high digestibility which suggests improved dietary attributes (**Nuwamanya et al., 2010**). The reduction in the swelling power of phthalated

starches is an important property for their applications in biodegradable films.

Table 1 shows the water solubility of native and modified starches. Native cocoyam starch has a solubility of $1.56 \pm 0.06 \text{ g.g}^{-1}$ which then increased after acetylation to $2.25 \pm 0.25 \text{ g.g}^{-1}$, and reduced after phthalation to $0.54 \pm 0.04 \text{ g.g}^{-1}$. The water solubility values for native white yam and bitter yam starches were 2.58 ± 0.06 and 2.18 ± 1.26 , respectively. There was an increase in the values after acetylation, a reduction in value was however observed after phthalation. The increase in water solubility of acetylated form could be due to the structural rearrangement which weakens the granules and improves amylose leaching (**Lawal, 2004**). Similar reports on water solubility on African yam bean and corn were submitted by (**Akintayo and Akintayo, 2009**) and (**Ayucitra, 2007**) starches. A decrease in water solubility after modification of Acha starch has been reported by **Olu-Owolabi et al. (2014)**.

The gelatinization temperatures of the native, acetylated and phthalated starches, are presented in Table 2. Acetylated and phthalated starches (cocoyam, whiteyam, and bitter yam) have lower gelatinization temperature compared to their corresponding native starches. These observations are in agreement with previous studies (**Lawal, 2011; Lee and Yoo, 2011**). A decrease in gelatinization temperatures could be traced to the phthalation and acetylation processes in the starch polymer backbone, which permits improved flexibility (**Singh, Chawla and Singh, 2004**). A decrease in gelatinization temperature is useful as a thickening agent in various industries, whereby the starch will form a gel at a lower temperature. However, thermal treatment reduced anti-nutritional agents (**Lauková et al., 2020**).

The pH values for acetylated and phthalated starches were found to be slightly lower than their corresponding native starches, but still fall within the pH range of 3 – 9 obtained for most starches used in pharmaceutical, domestic, and food industries. The reduction in pH of native starches after acetylation and phthalation can be attributed to the modification processes thereby increasing the acidity of starch molecules. The amylose content of native cocoyam starch ($20.90\% \pm 0.06$) was reduced ($18.73\% \pm 0.64$) after acetylation, and increased after phthalation ($30.31\% \pm 0.17$), amylose content of the native white yam ($21.53\% \pm 0.30$) and bitter yam ($22.73\% \pm 0.31$) decreased ($18.63\% \pm 0.17$; $31.37\% \pm 0.15$) after acetylation, and increased ($28.67\% \pm 0.38$; $27.53\% \pm 0.38$) after phthalation. Phthalated cocoyam starch showed the highest amylose content while acetylated white yam starch showed the least amylose content. The decrease in amylose content of acetylated starch was in agreement with the report of **Lawal (2004)**, on the reduction of amylose content of new cocoyam starch after acetylation. **Reddy, Haripriya and Suriya (2014)** also submitted a similar report on acetylated banana starch. Increased amylose contents of phthalated starches were in consonance with the report submitted by **Singh, Chawla and Singh (2004)** on modified potato and corn starches. Amylose content undergoes changes upon modification, also, structural differences between amylose and amylopectin can be considered as one of the most important factors of starch properties. Low amylose level makes starch a good source of food for diabetic and other

Table 1 Functional properties of native and modified starches.

| Sample | WAC (g.g ⁻¹) | OAC (g.g ⁻¹) | SWP (g.g ⁻¹) | Solubility (g.g ⁻¹) | Gelation temp. (°C) | Amylose content (%) | pH | Bulk density (g.mL ⁻¹) | Amylopectin % |
|----------------------------------|-----------------------------|-----------------------------|-----------------------------|------------------------------------|---------------------------|-----------------------------|------|--|--------------------------|
| Native cocoyam sample | 8.70 ±0.22 ^h | 2.57 ±0.21 ^c | 2.84 ±0.05 ^g | 1.56 ±0.06 ^d | 85 | 20.90 ±0.06 ^d | 6.50 | 0.61 ±0.08 ^a | 79.10 ±0.25 ^b |
| Acetylated yam sample | 9.37 ±0.15 ^k | 3.33 ±0.42 ^f | 4.39 ±0.20 ^k | 2.25 ±0.25 ^g | 78 | 18.73 ±0.64 ^b | 3.91 | 0.45 ±0.05 ^e | 81.27 ±0.24 ^d |
| Phthalated cocoyam sample | 6.50 ±0.30 ^c | 1.63 ±0.25 ^a | 1.84 ±0.05 ^c | 0.54 ±0.04 ^a | 80 | 30.31 ±0.17 ^k | 5.72 | 0.32 ±0.06 ^d | 69.69 ±0.05 ^e |
| Native white yam | 8.17 ±0.15 ^c | 3.47 ±0.06 ^h | 2.15 ±0.05 ^d | 2.58 ±0.06 ^h | 82 | 21.53 ±0.30 ^c | 6.20 | 0.65 ±0.22 ^h | 78.47 ±0.12 ^c |
| Acetylated white yam | 8.87 ±0.15 ^b | 4.53 ±0.06 ^l | 3.87 ±0.08 ^j | 3.00 ±0.08 ⁱ | 78 | 18.63 ±0.17 ^b | 4.52 | 0.69 ±0.03 ⁱ | 81.37 ±0.21 ^f |
| Phthalated white yam | 5.33 ±0.50 ^a | 3.37 ±0.21 ^g | 1.64 ±0.04 ^b | 1.50 ±0.16 ^c | 80 | 28.67 ±0.38 ^j | 5.67 | 0.53 ±0.08 ^f | 71.33 ±0.32 ^g |
| Native bitter yam | 8.94 ±0.05 ^j | 3.62 ±0.20 ⁱ | 3.70 ±0.25 ⁱ | 2.18 ±1.26 ^f | 82 | 22.73 ±0.31 ^f | 6.75 | 0.51 ±0.04 ^c | 77.27 ±0.51 ^b |
| Acetylated bitter yam | 8.50 ±0.27 ^g | 4.03 ±0.06 ^k | 4.63 ±0.15 ^l | 3.24 ±0.17 ^j | 74 | 21.37 ±0.15 ^g | 4.61 | 0.43 ±0.03 ^b | 78.63 ±0.22 ^d |
| Phthalated bitter yam | 7.56 ±0.21 ^d | 2.23 ±0.15 ^b | 2.61 ±0.15 ^e | 1.56 ±1.24 ^d | 80 | 27.53 ±0.38 ⁱ | 5.22 | 0.34 ±0.07 ^k | 72.47 ±0.05 ^h |

Note: Values are means of three replicates (determined on dry weight basis) ± standard deviation, significantly different at $p < 0.05$. WAC – water absorption capacity; OAC – oil absorption capacity; SWP – swelling power.

Table 2 Least gelation concentration of native and modified starches.

| Sample | 2% | 4% | 6% | 8% | 10% | 12% | 14% | 16% |
|----------------------------------|----------|----------|----------|-------|-------|-------|-------|-------|
| Native cocoyam sample | -Viscous | -Viscous | + Gel | + Gel | + Gel | + Gel | + Gel | + Gel |
| Acetylated yam sample | -Viscous | -Viscous | -Viscous | + Gel | + Gel | + Gel | + Gel | + Gel |
| Phthalated cocoyam sample | -Viscous | -Viscous | -Viscous | + Gel | + Gel | + Gel | + Gel | + Gel |
| Native white yam | -Viscous | -Viscous | + Gel | + Gel | + Gel | + Gel | + Gel | + Gel |
| Acetylated white yam | -Viscous | -Viscous | -Viscous | + Gel | + Gel | + Gel | + Gel | + Gel |
| Phthalated white yam | -Viscous | -Viscous | -Viscous | + Gel | + Gel | + Gel | + Gel | + Gel |
| Native bitter yam | -Viscous | -Viscous | + Gel | + Gel | + Gel | + Gel | + Gel | + Gel |
| Acetylated bitter yam | -Viscous | -Viscous | -Viscous | + Gel | + Gel | + Gel | + Gel | + Gel |
| Phthalated bitter yam | -Viscous | -Viscous | -Viscous | + Gel | + Gel | + Gel | + Gel | + Gel |

Note: Determination were carried out in triplicates. (-) No gelation and (+) gelation.

health conscious beings (Agbo and Odo, 2010). However, high amylose content often leads to retrogradation.

Table 1 shows the bulk density of native and modified starches. Native cocoyam starch has a bulk density of $0.61 \pm 0.08 \text{ g.g}^{-1}$, which decreased after both acetylation and phthalation to 0.45 ± 0.05 and $0.32 \pm 0.06 \text{ g.g}^{-1}$. The bulk density values of the native white yam and bitter yam starches (0.65 ± 0.22 and $0.51 \pm 0.04 \text{ g.g}^{-1}$) decreased after both acetylation (3.00 ± 0.08 and $3.24 \pm 0.17 \text{ g.g}^{-1}$) and phthalation (1.50 ± 0.16 and $1.56 \pm 1.24 \text{ g.g}^{-1}$). Native white yam starch has the highest bulk density of $0.65 \pm 0.22 \text{ g.g}^{-1}$, while phthalated cocoyam starch (0.32 ± 0.06) has the least bulk density. Acetylation and phthalation reduced the bulk density of the starches. The higher bulk density of a material, the more the quantity which can be packaged in a confined space (Fagbemi, 1999). Materials with high bulk density are regarded as heavy.

The results of the least gelation of native and modified starches are presented in Table 2. The lowest gelation concentration for native cocoyam, white yam, and bitter

yam starches was 6%. However, none of the starches showed positive results at the concentrations of 2 and 4%. At 8% concentration, all the native and modified starches formed a gel, all other higher concentrations showed positive results. It was observed that an increase in concentration leads to gel formation. A similar increase in the least gelation concentration upon acetylation was obtained in acetylated starches of African yambean starch (Akintayo and Akintayo, 2009) and sweet potato starch (Diop et al., 2011). Thus, the results suggested that the native starches are better gelating food additives than acetylated and phthalated starches.

CONCLUSION

It can be concluded that phthalation of native starches reduced water absorption capacity, swelling capacity, solubility, oil absorption capacity, swelling power, amylose content of the starches which are better properties of biodegradable polymers while acetylation increased

water absorption capacity, oil absorption capacity, swelling power and solubility of the starches which make the starches to be useful in confectioneries. This study, apart from establishing the characterization differences between native and modified starches has also provided information that the modified starches have more and improved applications in food industries.

REFERENCES

- Adebayo, A. S., Itiola, O. A. 1998. Evaluation of Breadfruit and Cocoyam Starches as Exodisintegrants in a Paracetamol Tablet Formulation. *Pharmacy Pharmacology Communications*, vol. 4, no. 8, p. 385-389.
- Adebowale, K. O., Lawal, O. S. 2003. Functional properties and retrogradation behaviour of native and chemically modified starch of mucuna bean (*Mucuna pruriens*). *Journal of the Science of Food and Agriculture*, vol. 83, p. 1541-1546. <https://doi.org/10.1002/jsfa.1569>
- Agbo, I. U., Odo, G. E. 2010. The Effect of Hypochlorite Oxidation and Acetylation on Some of the Physicochemical Properties of *Icacina Ttrichantha* Starch. *Bio-Research*, vol. 8, no. 1, p. 593-597. <https://doi.org/10.4314/br.v8i1.62539>
- Akintayo C. O., Akintayo, E. T. 2009. Preparation, Composition and Physico-chemical Characteristics of Native, Oxidized and Acetylated African Yambean (*Sphenostylis Sternocarpa*) Starches. *Advances in Natural and Applied Sciences*, vol. 3, no. 2, p. 196-203. Available at: <http://www.aensiweb.com/old/anas/2009/196-203.pdf>
- Attama, A. A., Nnamani, P. O., Mbonu, I. K., Adiku, M. U. 2003. Effect of hypochlorite oxidation on the physicochemical properties of gladiolus starch. *Journal of Pharmaceutical and allied Science*, vol. 1, p. 28-35.
- Awokoya, K. N., Nwokocha, L. M., Moronkola, B. A., Moronkola, D. O. 2011. Studies on the isolation, structural and functional properties of Starch Succinate of Cocoyam (*Colocasia antiquorum*). *Der Chemica Sinica*, vol. 2, no. 6, p. 228-244.
- Ayucitra, A. 2007. Preparation and Characterisation of Acetylated Corn Starches. *International Journal of Chemical Engineering and Applications*, vol. 3, no. 3, p. 152-159.
- Diop, C. I. K., Li, H. L., Xie, B. J., Shi, J. 2011. Effects of acetic acid/acetic anhydride ratios on the properties of corn starch acetates. *Food Chemistry*, vol. 126, no. 4, p. 1662-1669. <https://doi.org/10.1016/j.foodchem.2010.12.050>
- Dura, A., Rosell, C. M. 2016. Physico-chemical properties of corn starch modified with cyclodextrin glycosyltransferase. *International Journal of Biological Macromolecules*, vol. 87, p. 466-472. <https://doi.org/10.1016/j.ijbiomac.2016.03.012>
- Fagbemi, T. N. 1999. Effect of blanching and ripening on functional properties of plantain (*Musa aab*) flour. *Plant Foods for Human Nutrition*, vol. 54, p. 261-269. <https://doi.org/10.1023/A:1008153404357>
- Gbadamosi, S. O., Oladeji, B. S. 2013. Comparative studies of the functional and physico-chemical properties of isolated Cassava, Cocoyam and Breadfruit starches. *International Food Research Journal*, vol. 20, no. 5, p. 2273-2277.
- Gunaratne, A., Corke, H. 2007. Functional Properties of Hydroxypropylated, Cross-Linked, and Hydroxypropylated Cross-Linked Tuber and Root Starches. *Cereal Chemistry*, vol. 84, no. 1, p. 30-37. <https://doi.org/10.1094/CCHEM-84-1-0030>
- Lauková, M., Karovičová, J., Minarovičová, L., Kohajdová, Z. 2020. Effect of Thermal Stabilization on Physico-Chemical Parameters and Functional Properties of Wheat Bran. *Potravinarstvo Slovak Journal of Food Sciences*, vol. 14, no. 1, p. 170-177. <https://doi.org/10.5219/1321>
- Lawal, O. S. 2004. Composition, physicochemical properties and retrogradation characteristics of native, oxidised, acetylated and acid-thin new cocoyam (*Xanthosoma sagittifolium*) starch. *Food Chemistry*, vol. 87, no. 2, p. 205-218. <https://doi.org/10.1016/j.foodchem.2003.11.013>
- Lawal, O. S. 2011. Hydroxypropylation of pigeon pea (*Cajanus cajan*) starch: Preparation, functional characterizations and enzymatic digestibility. *LWT - Food Science and Technology*, vol. 44, no. 3, p. 771-778. <https://doi.org/10.1016/j.lwt.2010.05.025>
- Lee, H. L., Yoo, B. 2011. Effect of hydroxypropylation on physical and rheological properties of sweet potato starch. *LWT - Food Science and Technology*, vol. 44, no. 3, p. 765-770. <https://doi.org/10.1016/j.lwt.2010.09.012>
- Lee, H., Yoo, B. 2009. Dynamic Rheological and Thermal Properties of Acetylated Sweet Potato Starch. *Starch*, vol. 61, no. 7, p. 407-413. <https://doi.org/10.1002/star.200800109>
- Mano, J. F., Koniarova, D., Reis, R. L. 2003. Thermal properties of thermoplastic starch/synthetic polymer blends with potential biomedical applicability. *Journal of Materials Science: Materials in Medicine*, vol. 14, p. 127-135. <https://doi.org/10.1023/A:1022015712170>
- Medoua, G. N., Mbome, I. L., Agbor-Egbe, T., Mbofung, C. M. F. 2005. Study of the hard-to-cook property of stored yam tubers (*Dioscorea dumetorum*) and some determining biochemical factors. *Food Research International*, vol. 38, no. 2, p. 143-149. <https://doi.org/10.1016/j.foodres.2004.09.005>
- Mir, J. A., Srikaeo, K., Garcia, J. 2013. Effects of amylose and resistant starch on starch digestibility of rice flours and starches. *International Food Research Journal*, vol. 20, no.3, p. 1329-1335.
- Nuwamanya, E., Baguma, Y., Emmambux, N., Taylor, J., Rubaihayo, P. 2010. Physicochemical and functional characteristics of cassava starch in Ugandan varieties and their progenies. *Journal of Plant Breeding and Crop Science*, vol. 2, no. 1, 11 p.
- Olayinka, O. O., Adebowale, K. O., Olu-Owolabi, I. B. 2013. Physicochemical properties, morphological and X-ray pattern of chemically modified white sorghum starch (Bicolor-Moench). *Journal of Food Science and Technology*, vol. 50, no. 1, p. 70-77. <https://doi.org/10.1007/s13197-011-0233-3>
- Olu-Owolabi, B. I., Olayinka, O. O., Adegbemile, A. A., Adebowale, K. O. 2014. Comparison of Functional Properties between Native and Chemically Modified Starches from Acha (*Digitaria stapf*) Grains. *Food and Nutrition Sciences*, vol. 5, no. 2, p. 222-230. <https://doi.org/10.4236/fns.2014.52027>
- Omojola, M. O., Akinkunmi, Y. O., Olufunsho, K. O., Egharevba, H. O., Martins, E. O. 2010. Isolation and physico-chemical characterization of cola starch. *African Journal of Food, Agriculture, Nutrition and Development*, vol. 10, no. 7, p. 2884-2900. <https://doi.org/10.4314/ajfand.v10i7.59042>
- Omojola, M. O., Orishadipe, A. T., Afolayan, M. O., Adebisi, A. B. 2012. Preparation and physicochemical characterization of icacina starch citrate- a potential pharmaceutical / industrial starch. *Agriculture and Biology Journal of North America*, vol. 3, no. 1, p. 11-16. <https://doi.org/10.5251/abjna.2012.3.1.11.16>
- Omonigho, S. E., Ikenebomeh, M. J. 2000. Effects of different preservative treatments on the chemical changes of pounded white yam (*Dioscorea rotundata*) in storage at 28±2°C. *Food Chemistry*, vol. 68, no. 2, p. 201-209. [https://doi.org/10.1016/S0308-8146\(99\)00183-1](https://doi.org/10.1016/S0308-8146(99)00183-1)

- Owuamanam, C. I., Iwuoha, I. C., Onuegbu, C. N., Ogueke, C. C., Nwosu, J. N. 2013. Quality Characteristics of Processed Flours from Trifoliate Yam (*Dioscorea dumetorum*) as Influenced by Steeping and Boiling in Varying Concentration of Trona Solution over Time. *American Journal of Food Technology*, vol. 8, no. 3, p. 162-172. <https://doi.org/10.3923/ajft.2013.162.172>
- Reddy, C. K., Haripriya, S., Suriya, M. 2014. Effect of Acetylation on Morphology, Pasting and Functional Properties of Starch from banana (*Musa aab*). *Indian Journal of Scientific Research and Technology*, vol. 2, no. 6, p. 31-36.
- Sathe, S. K., Salunkhe, D. K. 1981. Isolation, Partial Characterization and Modification of Great Northern Bean (*Phaseolus vulgaris* L.) Starch. *Journal of Food Science*, vol. 46, no. 2, p. 617-621. <https://doi.org/10.1111/j.1365-2621.1981.tb04924.x>
- Shujun, W., Wenyuan, G., Wei, J., Peigen, X. 2006. Crystallography, morphology and thermal properties of starches from four different medicinal plants of Fritillaria species. *Food Chemistry*, vol. 96, no. 4, p. 591-596. <https://doi.org/10.1016/j.foodchem.2005.03.014>
- Singh, J., Kaur, L., Singh, N. 2004. Effect of Acetylation on Some Properties of Corn and Potato Starches. *Starch*, vol. 56, no. 12, p. 586-601. <https://doi.org/10.1002/star.200400293>
- Singh, N., Chawla, D., Singh, J. 2004. Influence of acetic anhydride on physicochemical, morphological and thermal properties of corn and potato starch. *Food Chemistry*, vol. 86, no. 4, p. 601-608. <https://doi.org/10.1016/j.foodchem.2003.10.008>
- Surini, S., Ssputri, K., Anwar, E. 2014. Preparation and characterization of praelatinized cassava starch Phthalate as a pH-sensitive polymer for enteric coated tablet formulation. *International Journal of Pharmacy and Pharmaceutical Science*, vol. 6, no. 3, p. 17-23.
- Tonukari, N. J. 2004. Cassava and the future of starch. *Electronic Journal of Biotechnology*, vol. 7, no. 1, 4 p. <https://doi.org/10.2225/vol7-issue1-fulltext-9>
- Torruco-Uco, J., Betancur-Ancona, D. 2007. Physicochemical and functional properties of makal (*Xanthosomayu catanensis*) starch. *Food Chemistry*, vol. 101, no. 4, p. 1319-1326. <https://doi.org/10.1016/j.foodchem.2006.03.047>
- Uzomah, A., Ibe, C. 2011. The functional properties, pasting and baking behaviour of chemically modified sour cassava starches. *African Journal of Food Science*, vol. 5, no. 12, p. 686-694.
- Wang, Y. J., Truong, V. D., Wang, L. 2003. Structures and rheological properties of corn starch as affected by acid hydrolysis. *Carbohydrate Polymers*, vol. 52, no. 3, p. 327-333. [https://doi.org/10.1016/S0144-8617\(02\)00323-5](https://doi.org/10.1016/S0144-8617(02)00323-5)
- Xu, Y. X., Dzenis, Y., Hanna, M. A. 2005. Water solubility, thermal characteristics and biodegradability of extruded starch acetate foams. *Industrial Crops and Products*, vol. 21, no. 3, p. 361-368. <https://doi.org/10.1016/j.indcrop.2004.05.004>
- Yadav, R., Garg, G. 2013. A review on Indian Sago Starch and its Pharmaceutical Applications. *International Journal of Pharmaceutical and Life Sciences*, vol. 2, no. 3, p. 99-106. <https://doi.org/10.3329/ijpls.v2i3.15456>
- Yu, W., He, H., Cheng, N., Gan, B., Li, X. 2009. Preparation and experiments for a novel kind of foundry core binder made from modified potato starch. *Materials and Design*, vol. 30, no. 1, p. 210-213. <https://doi.org/10.1016/j.matdes.2008.03.017>

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